11 The p-Block Elements

I. Multiple Choice Questions (Type-I)

1. The element which exists in liquid state for a wide range of temperature and can be used for measuring high temperature is

   (*i*) B (*ii*) Al
   (*iii*) Ga (*iv*) In

Ans. (*iii*)

Explanation: Gallium has different structure consisting Ga_2 molecule with lowest melting point. It exists as a liquid from 30°C to 2000°C and hence it is used in high temperature thermometry.

2. Which of the following is a Lewis acid?

   (*i*) $AlCl_3$ (*ii*) $MgCl_2$
   (*iii*) $CaCl_2$ (*iv*) $BaCl_2$

Ans. (*i*)

Explanation: Lewis acids are the species in which octate is not complete and ready to accept electrons. In $AlCl_3$, Al is surrounded by 6 electrons and all three Cl atoms are surrounded by 8 electrons, therefore, $AlCl_3$ is electron accepter. It is a covalent compound.

3. The geometry of a complex species can be understood from the knowledge of type of hybridisation of orbitals of central atom. The hybridisation of orbitals of central atom in $[Be(OH)_4]^-$ and the geometry of the complex are respectively

   (*i*) sp^3, tetrahedral (*ii*) sp^3, square planar
   (*iii*) sp^3d^2, octahedral (*iv*) dsp^2, square planar

Ans. (*i*)

Explanation: In$[B(OH)_4]^-$, Boron is surrounded by 4 bonds pair and has no lone pair. Geometry and hybridization of central atom is based on bond pairs and lone pairs around the central atom. $[B(OH)_4]^-$ is tetrahedral and Boron is sp^3 hybridized.

4. Which of the following oxides is acidic in nature?

   (*i*) B_2O_3 (*ii*) Al_2O_3
   (*iii*) Ga_2O_3 (*iv*) In_2O_3

Ans. (*i*)

Explanation: In group 13 (boron family) on moving down the group, acidic character decreases and basic character increases, therefore, B_2O_3 is acidic in nature.

5. The exhibition of highest co-ordination number depends on the availability of vacant orbitals in the central atom. Which of the following elements is not likely to act as central atom in MF_6^{3-}?

(*i*) B (*ii*) Al
(*iii*) Ga (*iv*) In

Ans. (*i*)

Explanation: Boron does not have *d*-orbital. The element M in the complex ion MF_6^{3-} has coordination number 6. Boron can have maximum coordination number 4. Thus, B cannot form this complex.

6. Boric acid is an acid because its molecule
   (*i*) contains replaceable H^+ ion
   (*ii*) gives up a proton
   (*iii*) accepts OH^- from water releasing proton
   (*iv*) combines with proton from water molecule

Ans. (*iii*)

Explanation: Boric acid is Lewis acid and accepts electron. It reacts with water and accepts OH^- and release H^+ ion and thus, acts as weak monobasic acid.

$$H_3BO_3 + H_2O \rightarrow B(OH)_4^- + H^+$$

7. Catenation i.e., linking of similar atoms depends on size and electronic configuration of atoms. The tendency of catenation in Group 14 elements follows the order:
   (*i*) C > Si > Ge > Sn (*ii*) C >> Si > Ge ≈ Sn
   (*iii*) Si > C > Sn > Ge (*iv*) Ge > Sn > Si > C

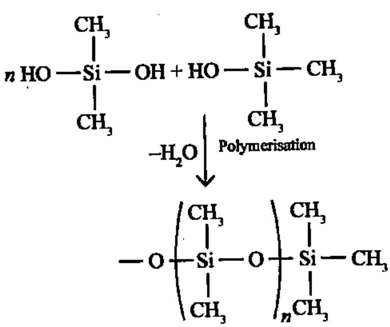
Ans. (*ii*)

Explanation: On moving down the group the size of the atom increases and the bond energy decreases and property of catenation decreases. In group 14 carbon shows maximum catenation. C >> Si > Ge ≈ Sn.

8. Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding
   (*i*) $MeSiCl_3$ (*ii*) Me_2SiCl_2
   (*iii*) Me_3SiCl (*iv*) Me_4Si

Ans. (*iii*)

Explanation: The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the ends as shown below:



Silicone

9. Ionisation enthalpy ($\Delta_i H_1$ kJ mol^{-1}) for the elements of Group 13 follows the order.

(*i*) B > Al > Ga > In > Tl (*ii*) B < Al < Ga < In < Tl
(*iii*) B < Al > Ga < In > Tl (*iv*) B > Al < Ga > In < Tl

Ans. (*iv*)

Explanation: Ionization enthalpy($\Delta_i H$) decreases down the group as the size of atom increases and screening effect. Al to Ga : Ionization enthalpy increases slightly because both nuclear charge and screening effect increases but due to poor shielding by *d*-electrons effective nuclear charge on valence electron is more as a result ionization enthalpy increases. On moving Ga to In again ionization enthalpy decreases due to shielding effect of *d*-electrons. On moving from In to Tl ionization enthalpy again increases because of poor shielding effect of 4f^- electrons. That is why effective nuclear charge increases and ionization enthalpy increases.

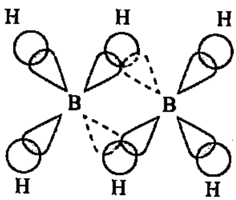
10. In the structure of diborane

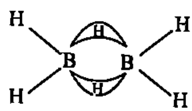
(*i*) All hydrogen atoms lie in one plane and boron atoms lie in a plane perpendicular to this plane.
(*ii*) 2 boron atoms and 4 terminal hydrogen atoms lie in the same plane and 2 bridging hydrogen atoms lie in the perpendicular plane.
(*iii*) 4 bridging hydrogen atoms and boron atoms lie in one plane and two terminal hydrogen atoms lie in a plane perpendicular to this plane.
(*iv*) All the atoms are in the same plane.

Ans. (*ii*)

Explanation: The four terminal hydrogen atoms and the two boron atoms lie in one plane.

Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two-centre-two-electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three-centre–two-electron bonds as shown in figure:





11. A compound X, of boron reacts with NH_3 on heating to give another compound Y which is called inorganic benzene. The compound X can be prepared by treating BF_3 with Lithium aluminium hydride. The compounds X and Y are represented by the formulas.

(*i*) B_2H_6, $B_3N_3H_6$ (*ii*) B_2O_3, $B_3N_3H_6$
(*iii*) BF_3, $B_3N_3H_6$ (*iv*) $B_3N_3H_6$, B_2H_6

Ans. (*i*)

Explanation: B_2H_6 reacts with ammonia and gives $B_2H_6.2NH_3$ which is formulated as $[BH_2(NH_3)_2]^+ [BH_4]^-$ and on heating gives $B_3N_3H_6$ borazine also called borazole.

$3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+ [BH_4]^- \xrightarrow{\text{Heat}} 2B_3N_3H_6 + 12H_2$

B_2H_6 can be prepared by reduction of BF_3 with $LiAlH_4$.

$4BF_3 + 3\ LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$

12. Quartz is extensively used as a piezoelectric material, it contains ________.

(*i*) Pb (*ii*) Si

(*iii*) Ti (*iv*) Sn

Ans. (*ii*)

Explanation: Quartz is one of the crystalline form of silica and at high temperature can be converted into other crystalline forms. It is extensively used as a piezoelectric material.

13. The most commonly used reducing agent is

(*i*) $AlCl_3$ (*ii*) $PbCl_2$

(*iii*) $SnCl_4$ (*iv*) $SnCl_2$

Ans. (*iv*)

Explanation: In $SnCl_2$, Sn^{2+} can be easily oxidised to Sn^{4+} because +4 oxidation state of Sn is more stable than +2 oxidation state. Hence, $SnCl_2$ acts as a reducing agent.

e.g., $SnCl_2 + 2FeCl_3 \rightarrow SnCl_4 + 2FeCl_2$

14. Dry ice is

(*i*) Solid NH_3 (*ii*) Solid SO_2

(*iii*) Solid CO_2 (*iv*) Solid N_2

Ans. (*iii*)

Explanation: Solid CO_2 is called dry ice because it is used for making ice bath for organic reaction in laboratory. It is prepared by cooling CO_2 gas at high pressure.

15. Cement, the important building material is a mixture of oxides of several elements. Besides calcium, iron and sulphur, oxides of elements of which of the group (s) are present in the mixture?

(*i*) group 2 (*ii*) groups 2, 13 and 14

(*iii*) groups 2 and 13 (*iv*) groups 2 and 14

Ans. (*ii*)

Explanation: Cement is manufactured by combining substances which are lime(CaO), clay contains Silica (SiO) and oxides of Al, Mg and iron.

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

16. The reason for small radius of Ga compared to Al is ________.

(*i*) poor screening effect of *d* and *f* orbitals

(*ii*) increase in nuclear charge

(*iii*) presence of higher orbitals
(*iv*) higher atomic number

Ans. (*i*) and (*ii*)

Explanation: On moving down the group from Al to Ga, the atomic radii decreases due to shielding effect of *d*-electrons. This effect is poor hence, effective nuclear charge increases.

17. The linear shape of CO_2 is due to ________.
(*i*) sp^3 hybridisation of carbon
(*ii*) *sp* hybridisation of carbon
(*iii*) $p\pi - p\pi$ bonding between carbon and oxygen
(*iv*) sp^2 hybridisation of carbon

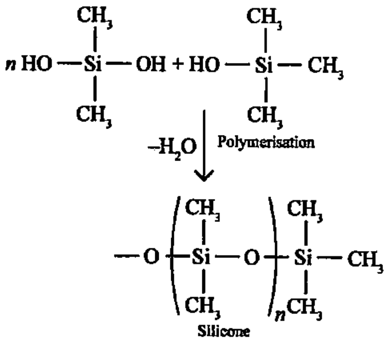
Ans. (*ii*) and (*iii*)

Explanation: Hybridization of C in CO_2 is sp and the structure is linear. Carbon is linked to two oxygen atoms through double bonds, one is sigma and other one is pi bond ($p\pi - p\pi$ bonding).

18. Me_3SiCl is used during polymerisation of organosilicones because
(*i*) the chain length of organosilicone polymers can be controlled by adding Me_3SiCl
(*ii*) Me_3SiCl blocks the end terminal of silicone polymer
(*iii*) Me_3SiCl improves the quality and yield of the polymer
(*iv*) Me_3SiCl acts as a catalyst during polymerisation

Ans. (*i*) and (*ii*)

Explanation: The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the ends.



19. Which of the following statements are correct?
(*i*) Fullerenes have dangling bonds
(*ii*) Fullerenes are cage-like molecules
(*iii*) Graphite is thermodynamically most stable allotrope of carbon
(*iv*) Graphite is slippery and hard and therefore used as a dry lubricant in machines

Ans. (*ii*) and (*iii*)

Explanation: Fullerenes are cage like molecules. C-60 molecule has the shape like a soccer ball and called **Buckminsterfullerene.**

Graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^\ominus$ of graphite is taken as zero. $\Delta_f H^\ominus$ values of diamond and fullerene, C-60 are 1.90 and 38.1 kJ mol^{-1}, respectively.

20. Which of the following statements are correct? Answer on the basis of Fig.11.1.

(*i*) The two birdged hydrogen atoms and the two boron atoms lie in one plane;

(*ii*) Out of six B–H bonds two bonds can be described in terms of 3-centre 2-electron bonds.

(*iii*) Out of six B-H bonds four B-H bonds can be described in terms of 3-centre 2-electron bonds;

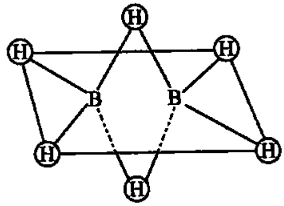
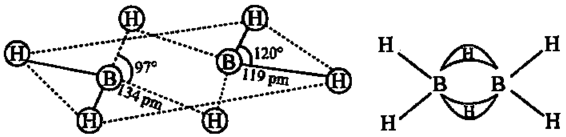


Fig. 11.1

(*iv*) The four terminal B-H bonds are two-centre-two-electron regular bonds.

Ans. (*i*), (*ii*) and (*iv*)

Explanation: The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre–two electron bonds.



21. Identify the correct resonance structures of carbon dioxide from the ones given below:

(*i*) $O-C\equiv O$ (*ii*) $O=C=O$

(*iii*) $^-O\equiv C-O^+$ (*iv*) $^-O-C\equiv O^+$

Ans. (*ii*) and (*iv*)

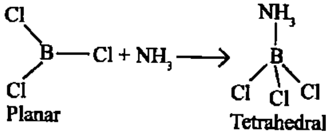
Explanation: $:\overset{-}{\ddot{\underset{\cdot\cdot}{O}}}-C\equiv\overset{+}{O}: \leftrightarrow :\ddot{O}=C=\ddot{O}: \leftrightarrow :\overset{+}{O}\equiv C-\overset{-}{\ddot{\underset{\cdot\cdot}{O}}}:$

Resonance explains delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by one single Lewis formula.

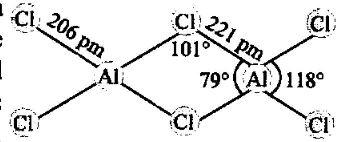
III. Short Answer Type

22. Draw the structures of $BCl_3.NH_3$ and $AlCl_3$ (dimer).

Ans. BCl_3 is covalent in nature and it is Lewis acid because octate of Boron is not completed. Boron needs a pair of electrons. It is sp^2 hybridized and triangular planar. Such electron deficient molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group. BCl_3 easily accepts a lone pair of electrons from ammonia to form $BCl_3.NH_3$.



$AlCl_3$ achieves stability by forming a dimer. In trivalent state most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hyrolysis in water form tetrahedral $M(OH)_4^-$. Element M is sp^3 hybridized and has tetrahedral shape.



Tetrahedral

23. Explain the nature of boric acid as a Lewis acid in water.

Ans. Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion:

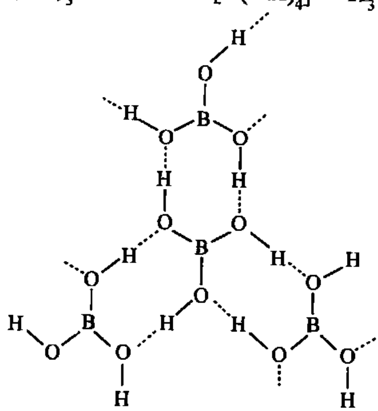
$$B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H_3O^+$$

24. Draw the structure of boric acid showing hydrogen bonding. Which species is present in water? What is the hybridisation of boron in this species?

Ans. It has a layer structure in which planar H_3BO_3 units are joined by hydrogen bonds forming hexagonal rings. Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion.

In water, boric acid is present in the form of $[B(OH)_4]^-$ species. The hybridisation of boron in this species is sp^3.

$$B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H_3O^+$$



25. Explain why the following compounds behave as Lewis acids?

(*i*) BCl_3 (*ii*) $AlCl_3$

Ans. In both the species, the central atom *i.e.*, Boron and Aluminium are surrounded by 6 electrons and each Cl atom in both is surrounded by 8 electrons. BCl_3 and $AlCl_3$ are electron-deficient and ready to accept a pair of electrons. Hence, they act as Lewis acids.

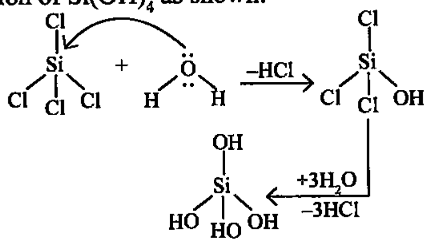
26. Give reasons for the following:

(*i*) CCl_4 is immiscible in water, whereas $SiCl_4$ is easily hydrolysed.

(*ii*) Carbon has a strong tendency for catenation compared to silicon.

Ans. (*i*) CCl_4 is a covalent compound and cannot form H—bond with polar H_2O and C does not have *d* orbital to accommodate the lone pair of electrons from oxygen atom of water molecule. Other tetra-chlorides are easily hydrolyzed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in *d* orbital.

Hydrolysis can be understood by taking the example of $SiCl_4$. It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in *d* orbitals of Si, finally leading to the formation of $Si(OH)_4$ as shown:



Silicic acid

(*ii*) Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is because C—C bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is C >> Si > Ge ≈ Sn. Lead does not show catenation.

Bond	Bond enthalpy/kJ mol^{-1}
C—C	348
Si—Si	297
Ge—Ge	260
Sn—Sn	240

27. Explain the following :

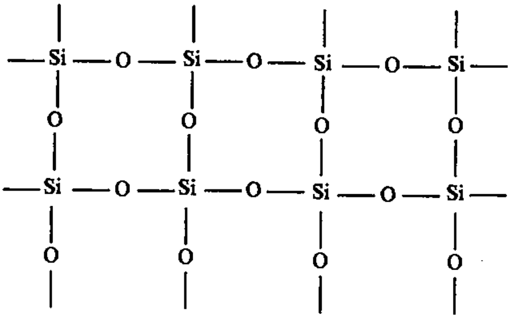
(*i*) CO_2 is a gas whereas SiO_2 is a solid.

(*ii*) Silicon forms SiF_6^{2-} ion whereas corresponding fluoro compound of carbon is not known.

Ans. (*i*) In CO_2, carbon atom undergoes *sp* hybridization. Two *sp* hybridized orbitals of carbon atom overlap with two *p* orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in $p\pi - p\pi$ bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment.

$$:\ddot{O}=C=\ddot{O}:$$

Silicon dioxide is a covalent, three-dimensional network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms as shown in diagram. Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternate silicon and oxygen atoms.



(*ii*) Silicon has vacant d orbital in its valence shell due to which it can accommodate 6 electrons from 6 fluorine atoms whereas carbon does not have d orbital and cannot expand its covalence beyond four.

28. The +1 oxidation state in group 13 and +2 oxidation state in group 14 becomes more and more stable with increasing atomic number. Explain.

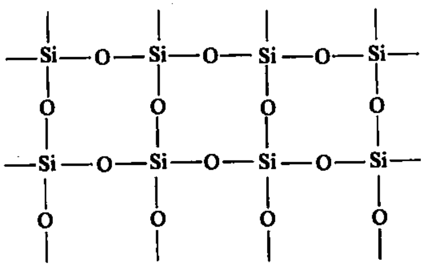
Ans. On moving down the group in group13 and 14, lower oxidation state becomes more stable as compared to higher oxidation state, because of inert pair effect. In inert pair effect '*s*' electrons of valence shell do not participate in bonding only '*p*' electrons participate in bonding. As the size of atom increases, more energy is needed by '*s*' electrons to participate in bonding from valence shell. In group 13 valence shell configuration is ns^2np^1 (n = 2 to 6), when electrons of both '*s*' and '*p*' orbitals participate they show +3 oxidation state but, if only '*p*' electrons participate then they show +1 oxidation state. In group 14 valence shell configuration is ns^2np^2 (n = 2 to 6), when electrons of both '*s*' and '*p*' orbitals participate then +4 oxidation state and if only '*p*' electrons participate, then +2 oxidation.

29. Carbon and silicon both belong to the group 14, but inspite of the stoichiometric similarity, the dioxides, (i.e., carbon dioxide and silicon dioxide), differ in their structures. Comment.

Ans. In CO_2, carbon atom undergoes *sp* hybridization. Two *sp* hybridized orbitals of carbon atom overlap with two *p* orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in $p\pi - p\pi$ bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment. Carbon can give double bond with oxygen due to its small size.

$$:\ddot{\underset{..}{O}}^{-}-C\equiv O^{+}: \leftrightarrow :\ddot{O}=C=\ddot{O}: \leftrightarrow :O^{+}\equiv C-\ddot{\underset{..}{O}}^{-}:$$

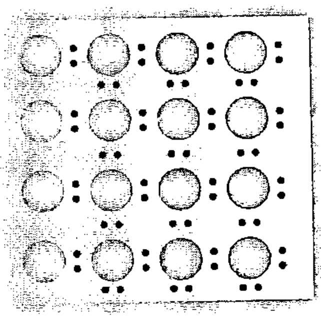
Silicon dioxide is a covalent, three-dimensional network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms as shown in diagram. Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternate silicon and oxygen atoms. Silicon cannot give double bond with oxygen due to large size and less electronegativity.



30. If a trivalent atom replaces a few silicon atoms in three dimensional network of silicon dioxide, what would be the type of charge on overall structure?

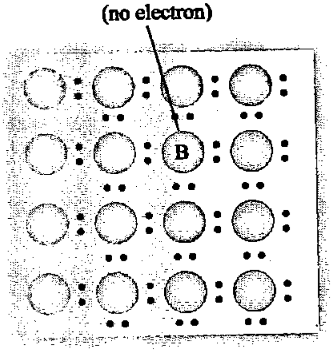
Ans. In SiO_2 structure, if a trivalent atom replaces Si atom, then holes are created. These holes will make the crystal, conductor of electricity, called *p*-type conduction. The crystals as whole are electrically neutral.

Silicon atom



Perfect crystal

Positive hole (no electron)



p-type

31. When BCl_3 is treated with water, it hydrolyses and forms $[B(OH)_4]^-$ only whereas $AlCl_3$ in acidified aqueous solution forms $[Al(H_2O)_6]^{3+}$ ion. Explain what is the hybridisation of boron and aluminium in these species?

Ans. In trivalent state, most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hydrolysis in water form tetrahedral $[M(OH)_4]^-$ species; the hybridization state of element M is sp^3. Aluminium chloride in acidified aqueous solution forms octahedral $[Al(H_2O)_6]^{+3}$ ion. In this complex ion, the 3d orbitals of Al are involved and the hybridisation state of Al is sp^3d^2.

32. Aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character. A piece of aluminium foil is treated with dilute hydrochloric acid or dilute sodium hydroxide solution in a test tube and on bringing a burning matchstick near the mouth of the test tube, a pop sound indicates the evolution of hydrogen gas. The same activity when performed with concentrated nitric acid, reaction doesn't proceed. Explain the reason.

Ans. Aluminium is amphoteric in nature, it reacts with acid and base to give salt and H_2 gas. It burns with pop sound.

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2(g)$$

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2(g)$$

When Al reacts with conc. HNO_3, a thin layer of Al_2O_3 on the surface of Al metal which protect further reaction. This layer is called protective layer.

$$2Al + 6HNO_3 \text{ conc.} \rightarrow Al_2O_3 + 6NO_2 + 3H_2O$$

33. Explain the following:

(*i*) Gallium has higher ionisation enthalpy than aluminium.

(*ii*) Boron does not exist as B^{3+} ion.

(*iii*) Aluminium forms $[AlF_6]^{3-}$ ion but boron does not form $[BF_6]^{3-}$ ion.

(*iv*) PbX_2 is more stable than PbX_4.

(*v*) Pb^{4+} acts as an oxidising agent but Sn^{2+} acts as a reducing agent.

(*vi*) Electron gain enthalpy of chlorine is more negative as compared to fluorine.

(*vii*) $Tl(NO_3)_3$ acts as an oxidising agent.

(*viii*) Carbon shows catenation property but lead does not.

(*ix*) BF_3 does not hydrolyse.

(*x*) Why does the element silicon, not form a graphite like structure whereas carbon does.

Ans. (*i*) The ionisation enthalpy value of Ga is higher than Al due to inability of *d*- and *f*-electrons, which have low screening effect, to compensate the increase in nuclear charge.

(*ii*) Boron has small size and sum of $\Delta_i H_1 + \Delta_i H_2 + \Delta_i H_3$ is very high. Boron does not form B^{3+} ion therefore, give covalent compounds.

(*iii*) Al has vacant '*d*' orbitals and can expand its co-ordination no. and forms $[AlF_6]^{3-}$. On the other hand, Boron does not have '*d*' orbitals and cannot form $[BF_6]^{3-}$ and cannot expand its covalence beyond 4 and thus, gives $[BF_4]^-$.

(*iv*) Due to inert pair effect, +2 oxidation state is more stable than +4 oxidation state.

(*v*) Pb^{4+} by gaining 2 electrons changes into Pb^{2+} which is more stable due to inert pair effect. Sn^{2+} is less stable than Sn^{4+} by loosing electrons. Therefore, Pb^{4+} acts as an oxidizing agent while Sn^{2+} acts as a reducing agent.

(*vi*) The size of F atom is very small and incoming electrons feel interelectronic repulsion and electron gain enthalpy of F is less negative as compared to Cl.

(*vii*) Due to inert pair effect, Tl is more stable in +1 oxidation state than that of +3 oxidation state. Therefore, $Tl(NO_3)_3$ acts as strong oxidizing agent.

(*viii*) Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is because C—C bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is C > > Si > Ge ≈ Sn. Lead does not show catenation.

(*ix*) BF_3 does not hydrolyse completely. It forms boric acid and fluoroboric acid this is because the HF formed reacts with H_3BO_3.

$$BF_3 + 3H_2O \rightarrow H_3BO_3 + 3HF \} \times 4$$
$$H_3BO_3 + 3HF \rightarrow H^+[BF_4]^- + 3\ H_2O \} \times 3$$
$$4\ BF_3 + 3H_2O \rightarrow H_3BO_3 + 3[BF_4]^- + 3H^+$$

(*x*) In graphite, carbon is sp^2 hybridized. Carbon has a tendency to form multiple pπ-pπ bonds due to its small size and highest electronegativity in group 14. Silicon due to its large size and less electronegativity cannot form multiple bonds. Thus, silicon can not form graphite like structure.

34. Identify the compounds A, X and Z in the following reactions:

(*i*) $A + 2HCl + 5H_2O \rightarrow 2NaCl + X$

$$X \xrightarrow[370\,K]{\Delta} HBO_2 \xrightarrow[>370\,K]{\Delta} Z$$

Ans. (*i*) $Na_2B_4O_7(A) + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3\ (X)$

$$H_3BO_3(X) \xrightarrow[370\,K]{\Delta} HBO_2 \xrightarrow[370\,K]{\Delta} B_2O_3\,(Z)$$

$Na_2B_4O_7(A)$, $H_3BO_3(X)$ and $B_2O_3(Z)$

35. Complete the following chemical equations:

$Z + 3LiAlH_4 \rightarrow X + 3LiF + 3AlF_3$

$X + 6H_2O \rightarrow Y + 6H_2$

$3X + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$

Ans.

$4BF_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$

$B_2H_6(g) + 6H_2O(l) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$

$B_2H_6 + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$

$Z = BF_3$, $X = B_2H_6$ and $Y = B(OH)_3$ or H_3BO_3

IV. Matching Type

In the following questions more than one correlation is possible between options of Column I and Column II. Make as many correlations as you can.

36. Match the species given in Column I with the properties mentioned in Column II.

Column I	Column II
(*i*) BF_4^-	(*a*) Oxidation state of central atom is +4
(*ii*) $AlCl_3$	(*b*) Strong oxidising agent
(*iii*) SnO	(*c*) Lewis acid
(*iv*) PbO_2	(*d*) Can be further oxidised
	(*e*) Tetrahedral shape

Ans. (*i*) → (*e*); (*ii*) → (*c*); (*iii*) → (*d*); (*iv*) → (*a*), (*b*)

Explanation:

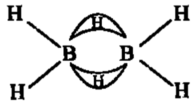
Column I	Column II
(*i*) BF_4^-	In BF_4^-, B is sp^3 hybridized and surrounded by 4 bond pairs and has no lone pair.
(*ii*) $AlCl_3$	In $AlCl_3$ octet of Al is not complete, electron deficient compound.
(*iii*) SnO	In SnO oxidation state of Sn is +2 and can be changed in to +4.
(*iv*) PbO_2	In PbO_2, oxidation state of Pb is +4, it is less stable due to inert pair effect and +2 oxidation state is more stable. Pb^{4+} changes into Pb^{2+} acts as a strong oxidizing agent.

37. Match the species given in Column I with properties given in Column II.

Column I	Column II
(*i*) Diborane	(*a*) Used as a flux for soldering metals
(*ii*) Gallium	(*b*) Crystalline form of silica
(*iii*) Borax	(*c*) Banana bonds
(*iv*) Aluminosilicate	(*d*) Low melting, high boiling, useful for measuring high temperatures
(*v*) Quartz	(*e*) Used as catalyst in petrochemical industries.

Ans. (*i*) → (*c*); (*ii*) → (*d*); (*iii*) → (*a*); (*iv*) → (*e*); (*v*) → (*b*)

Explanation:

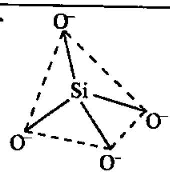
Column I	Column II
(*i*) Diborane	In B_2H_6, Each B atom uses sp^3 hybrids for bonding. Out of the four sp^3 hybrids on each B atom, one is without an electron shown in broken lines.  The terminal B-H bonds are normal 2-centre-2-electron bonds but the two bridge bonds are 3-centre-2-electron bonds. The 3-centre-2-electron bridge bonds are also referred to as banana bonds.
(*ii*) Gallium	Gallium with unusually low melting point (303K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures.
(*iii*) Borax	Borax is used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthen wares.
(*iv*) Aluminosilicate	Zeolites are aluminosilicates and widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, *e.g.*, ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline.
(*v*) Quartz	Quartz, cristobalite and tridymite are some of the crystalline forms of silica.

38. Match the species given in Column I with the hybridisation given in Column II.

Column I	Column II
(*i*) Boron in $[B(OH)_4]^-$	(*a*) sp^2
(*ii*) Aluminium in $[Al(H_2O)_6]^{3+}$	(*b*) sp^3
(*iii*) Boron in B_2H_6	(*c*) sp^3d^2
(*iv*) Carbon in Buckminsterfullerene	
(*v*) Silicon in SiO_4^{4-}	
(*vi*) Germanium in $[GeCl_6]^{2-}$	

Ans. (*i*) → (*b*); (*ii*) → (*c*); (*iii*) → (*b*); (*iv*) → (*a*); (*v*) → (*b*); (*vi*) → (*c*)

Explanation:

Column I	Column II
(*i*) Boron in $[B(OH)_4]^-$	Boron is central atom and is surrounded by 4 bond pairs only.
(*ii*) Aluminium in $[Al(H_2O)_6]^{3+}$	In $[Al(H_2O)_6]^{3+}$, coordination number of Al is 6 and geometry is octahedral.
(*iii*) Boron in B_2H_6	In B_2H_6, each B atom uses sp^3 hybrid orbitals for bonding. Out of the four sp^3 hybrids on each B atom, one is without an electron.
(*iv*) Carbon in Buckminsterfullerene	All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms.
(*v*) Silicon in SiO_4^{4-}	The basic structural unit of silicates is SiO_4^{4-}, in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion. 
(*vi*) Germanium in $[GeCl_6]^{2-}$	In $[GeCl_6]^{2-}$, Ge has coordination number 6 and it has octahedral geometry and central atom Ge is sp^3d^2 hybridised.

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

39. **Assertion (A) :** If aluminium atoms replace a few silicon atoms in three dimensional network of silicon dioxide, the overall structure acquires a negative charge.

    Reason (R) : Aluminium is trivalent while silicon is tetravalent.

    (*i*) Both A and R are correct and R is the correct explanation of A.
    (*ii*) Both A and R are correct but R is not the correct explanation of A.
    (*iii*) Both A and R are not correct
    (*iv*) A is not correct but R is correct.

Ans. (*iv*)

Explanation: Al is trivalent and Si is tetravalent and Reason is correct. Here the silicon is doped with gr. 13 element.

40. **Assertion (A) :** Silicons are water repelling in nature.

    Reason (R) : Silicons are organosilicon polymers, which have $(-R_2SiO-)$ as repeating unit.

(*i*) A and R both are correct and R is the correct explanation of A.
(*ii*) Both A and R are correct but R is not the correct explanation of A.
(*iii*) A and R both are not true.
(*iv*) A is not true but R is true.

Ans. (*ii*)

Explanation: Silicones are the group of silicon polymers, which have (R_2SiO) as a repeating unit. Silicones being surrounded by non-polar alkyl groups are water repelling in nature so A and R both are correct but R is not the correct explanation of A.

VI. Long Answer Type

41. Describe the general trends in the following properties of the elements in Groups 13 and 14.

(*i*) Atomic size
(*ii*) Ionisation enthalpy
(*iii*) Metallic character
(*iv*) Oxidation states
(*v*) Nature of halides

Ans. Group 13

(*i*) **Atomic size:** On moving down the group the size of atom increases because for each successive member of the group one extra shell of electrons is added but in some cases deviation is seen. The size of Ga is less than that of Al due to the poor shielding effect of 10 electrons present in d orbital.

(*ii*) **Ionisation enthalpy:** The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group. The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of *d*- and *f*-electrons, which have low screening effect, to compensate the increase in nuclear charge.

(*iii*) **Metallic character:** Boron is non metallic and all other elements are metallic. Metallic character increases from B to Al but from Al to Tl it decreases due to poor shielding effect of *d*-electrons and *f*-electrons.

(*iv*) **Oxidation states:** All elements show +3 oxidation state but on moving down the group due to inert pair effect +3 oxidation state decreases and +1 oxidation state progressively increases in the order of Al< Ga < In < Tl.

(*v*) **Nature of Halides:** These elements react with halogens to form trihalides (except TlI_3).

$$2E(s) + 3X_2(g) \rightarrow 2EX_3(s)\ (X = F, Cl, Br, I)$$

Halides of Boron and Aluminium are electron deficient and act as Lewis acids. Lewis acidic character of halides of boron decreases in the following order:

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

Group-14

(*i*) **Atomic size:** In group 14 atomic radius is referred as covalent radius. There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled *d* and *f* orbitals in heavier members due to screening effect.

(*ii*) **Ionisation Enthalpy:** The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general, the ionization enthalpy decreases down the group. Small decrease in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effect of intervening *d* and *f* orbitals and increase in size of the atom.

(*iii*) **Metallic character:** In group 14, on moving down the metallic character increases. Carbon is non-metal, Si and Ge are metalloid and Sn and Pb are metals.

(*iv*) **Oxidation states:** The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since, the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb.

It is due to the inability of ns^2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group. Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 state and only few compounds in +2 state.

(*v*) **Nature of Halides:** These elements can form halides of formula MX_2 and MX_4 (X = F, Cl, Br, I). Except carbon, all other members react directly with halogen under suitable conditions to make halides. Most of the compounds (MX_4) are covalent in nature. The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape. Exceptions are SnF_4 and PbF_4, which are ionic in nature. PbI_4 does not exist because Pb—I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. Heavier members Ge to Pb are able to make halides of formula MX_2.

42. Account for the following observations:

(*i*) $AlCl_3$ is a Lewis acid.

(*ii*) Though fluorine is more electronegative than chlorine yet BF_3 is a weaker Lewis acid than BCl_3.

(*iii*) PbO_2 is a stronger oxidising agent than SnO_2.

(*iv*) The +1 oxidation state of thallium is more stable than its +3 state.

Ans. (*i*) In $AlCl_3$, the octet of Al is incomplete as it has 6 electrons and accepts pair of electrons. Electron accepters are Lewis acids.

(*ii*) In BF_3, boron has a vacant 2*p* orbital and fluorine has one of the 2*p* orbital completely filled and unutilized. Both have same energy and can overlap effectively to give $p\pi$—$p\pi$ bond. This type of bonding called back bonding. Back bonding is strong in F and decreases down the Gp 17 as the size of halogens increases. Thurst of electrons of Boron is going to be fulfilled by back bonding.

(*iii*) It is more stable and acts as oxidizing agent. On moving down a group, inert pair effect increases and it is very strong in case of Pb therefore, PbO_2 is stronger oxidizing agent.

(*iv*) It is due to inert pair effect.

43. When aqueous solution of borax is acidified with hydrochloric acid, a white crystalline solid is formed which is soapy to touch. Is this solid acidic or basic in nature? Explain.

Ans. An aqueous solution of borax is acidified with HCl to give boric acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3$$

Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion:

$$B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H_3O^+$$

44. Three pairs of compounds are given below. Identify that compound in each of the pairs which has group 13 element in more stable oxidation state. Give reason for your choice. State the nature of bonding also.

(*i*) $TlCl_3$, TlCl (*ii*) $AlCl_3$, AlCl (*iii*) $InCl_3$, InCl

Ans. (*i*) TlCl is more stable than $TlCl_3$ because moving down the group lower oxidation state is more stable due to inert pair effect.

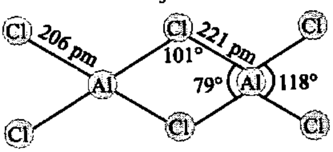
(*ii*) $AlCl_3$ is more stable because it does not show inert pair effect. It is a covalent compound and acts as a Lewis acid.

(*iii*) InCl is more stable due to inert pair effect and lower oxidation state +1 is more stable. In shows both the oxidation states +3 and +1.

45. BCl_3 exists as monomer whereas $AlCl_3$ is dimerised through halogen bridging.

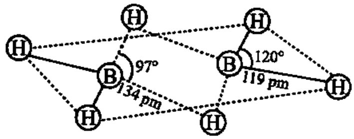
Give reason. Explain the structure of the dimer of $AlCl_3$ also.

Ans. BCl_3 does not dimerise because of its small size. BCl_3 do not exist as a dimer. Boron cannot accommodate four large sized chloride ions. $AlCl_3$ exist as a dimer in which Al uses its vacant 3*p*-orbital by coordinate with Cl to complete their octet by forming dimer. $AlCl_3$ achieves stability by forming a dimer.



Tetrahedral

46. Boron fluoride exists as BF_3 but boron hydride doesn't exist as BH_3. Give reason. In which form does it exist? Explain its structure.

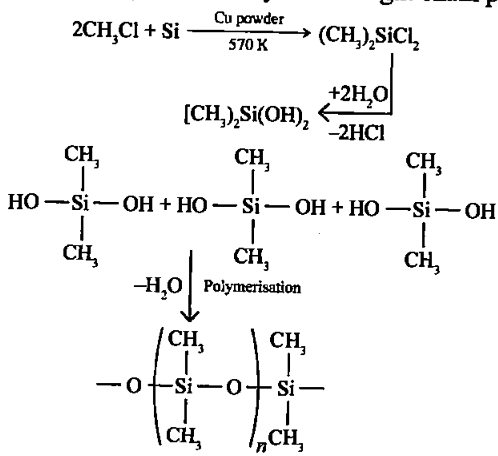


Ans. In BF_3, lone pair of fluorine gives back support of electrons to boron atom ($p\pi$—$p\pi$ back bonding). This delocalization of electrons reduces the deficiency of electrons and thus reduces Lewis acidic character and increases stability of BF_3. In BH_3, there is no lone pair of electrons on H atom, therefore, BH_3 dimerises to give B_2H_6. 4 terminal H atoms and 2 boron atoms lie in one plane and above and below the plane there are two bridging H atoms.

47. (*i*) What are silicones? State the uses of silicones.

(*ii*) What are boranes? Give chemical equation for the preparation of diborane.

Ans. (*i*) Silicones are a group of organosilicon polymers, which have (R_2SiO) as a repeating unit. The starting materials for the manufacture of silicones are alkyl or aryl substituted silicon chlorides, $RnSiCl_{(4-n)}$, where R is alkyl or aryl group. When methyl chloride reacts with silicon in the presence of copper as a catalyst at a temperature 573K various types of methyl substituted chlorosilane of formula $MeSiCl_3$, Me_2SiCl_2, Me_3SiCl with small amount of Me_4Si are formed. Hydrolysis of dimethyldichlorosilane, $(CH_3)_2SiCl_2$ followed by condensation polymerisation yields straight chain polymers.



Silicone

Uses: They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

(*ii*) Boranes are the binary compounds of boron and hydrogen like alkanes. These are covalent hydrides of formula B_2H_6 called diborane.

Preparation of diborane:

$$4BF_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

48. A compound (A) of boron reacts with NMe_3 to give an adduct (B) which on hydrolysis gives a compound (C) and hydrogen gas. Compound (C) is an acid.

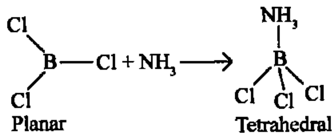
Identify the compounds A, B and C. Give the reactions involved.

Ans. Compound [A] of boron reacts with NMe_3 and gives an adduct [B] thus compound [A] is Lewis acid . Since] B] on hydrolysis gives an acid [C] and H_2 gas, therefore [A] is B_2H_6, [B] is an adduct $2BH_3NMe_3$ and [C] is boric acid. Reactions are as follows:

$$B_2H_6(A) + 2NMe_3 \rightarrow 2BH_3NMe_3(B)$$
$$BH_3NMe_3 + 3H_2O \rightarrow H_3BO_3(C) + NMe_3 + 6H_2$$

49. A nonmetallic element of group 13, used in making bullet proof vests is extremely hard solid of black colour. It can exist in many allotropic forms and has unusually high melting point. Its trifluoride acts as Lewis acid towards ammonia. The element exihibits maximum covalency of four. Identify the element and write the reaction of its trifluoride with ammonia. Explain why does the trifluoride act as a Lewis acid.

Ans. In group 13, boron is only non-metallic and extremely hard and also used for making bullet proof vests. Boron exists in many allotropic forms. It usually shows high melting point and does not have '*d*' orbital. It can show maximum covalence of 4 by using 2*s* and 2*p* orbitals. In trivalent halides of boron, octet of boron is not completed hence acts as Lewis acid. It reacts with Lewis base and forms adduct.



50. A tetravalent element forms monoxide and dioxide with oxygen. When air is passed over heated element (1273 K), producer gas is obtained. Monoxide of the element is a powerful reducing agent and reduces ferric oxide to iron. Identify the element and write formulas of its monoxide and dioxide. Write chemical equations for the formation of producer gas and reduction of ferric oxide with the monoxide.

Ans. Producer gas is a mixture of $CO(g)$ and $N_2(g)$. Carbon is tetravalent and gives monoxide (CO) and dioxide (CO_2) with oxygen.

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273\,K} \underbrace{2CO(g) + 4N_2(g)}_{\text{Producer gas}}$$

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{Heat} 2Fe(s) + 3CO_2(g)$$

❑❑❑